

IRREVERSIBLE THERMODYNAMICS FOR QUANTUM SYSTEMS WEAKLY COUPLED TO THERMAL RESERVOIRS

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CONTENTS

I. Introduction	109
II. The Microscopic Model	111
III. The Weak Coupling Limit	118
IV. Detailed Balance and the KMS Condition	123
V. Entropy Production	127
VI. Approach to Stationarity	133
VII. Onsager Relations	134
VIII. Principle of Minimal Entropy Production	137
References	140

I. INTRODUCTION

Statistical mechanics is the link between the microscopic and macroscopic world. Put more poetically—since this article is dedicated to Ilya Prigogine, whose life is devoted to the discovery and exposition of the grand poetry of nature—statistical mechanics is the bridge between the

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world of the atom and the world of the object. Man lives in the latter world but wishes, for aesthetic as well as for practical reasons, to understand the relation between the two worlds. This is the task of statistical mechanics.

Traditionally, statistical mechanics is split into two parts: equilibrium and nonequilibrium. Our understanding of the former is, formally at least, essentially complete. The Gibbs formalism gives a well-specified prescription for computing all the equilibrium properties of a macroscopic system from a knowledge of its microscopic Hamiltonian. Compared to this, our understanding of nonequilibrium statistical mechanics is still very incomplete. There is no general prescription for computing from first principles the great variety of nonequilibrium behavior observed in macroscopic systems. Some progress has been made, however, in recent years, and Prigogine is one of the pioneers in this field. It is therefore appropriate that this article, which describes recent developments in one small corner of this vast field, should be dedicated to him on the occasion of his sixtieth birthday.

The nonequilibrium phenomena we shall deal with in this article are transport processes. We wish to find the "Gibbs ensemble" appropriate for the description of a system in which there are flows of energy or material. Unfortunately, no such prescription exists at the present time even if we restrict ourselves to the case of steady fluxes. It is only in the special case of the weak coupling or van Hove limit that a mathematically precise microscopic theory has been developed. This theory is applied here to the case of systems coupled weakly to several idealized heat reservoirs. Some new results concerning entropy production in such situations are also presented. This yields in some special cases a microscopic justification for the principle of minimal entropy production that Prigogine has used so effectively in the thermodynamics of irreversible processes.

The situation we consider, then, is that of a finite system (say, a metal bar) coupled to inexhaustible heat reservoirs (heating the metal bar at one end and cooling it at the other). The case, where the reservoirs are of a certain stochastic nature, has been studied in detail by Lebowitz et al.¹⁻⁴ To obtain a truly dynamical model we choose in the present paper as reservoirs (infinitely extended) ideal gases at equilibrium. Even with such a simplifying assumption very little can be said. Already the problem to show the existence of a steady heat transporting state can be solved only in very special cases (such as the harmonic chain); even worse, these examples all show anomalous transport properties (their heat conductivity is infinite). Only in the limit, where the coupling between the system and the reservoirs becomes weak (van Hove limit) does the situation improve. However, a price has to be paid: All quantities can be determined only to lowest nonvanishing order in the coupling constant λ . For example, the total

amount of energy flowing through the system $\langle J \rangle_\lambda$ has an expansion of the form $\langle J \rangle_\lambda = \lambda^2 \langle J_2 \rangle + \dots$. In the weak coupling limit $\langle J_2 \rangle$ can be determined.

In the limit of weak coupling we can prove the approach to a steady state as $t \rightarrow \infty$, the Onsager relations and the principle of minimal entropy production. Our proofs are based on two fundamental properties of the time evolution (which is a quantum generalization of a classical Markov process) obtained in this limit: (1) the detailed balance property, which is a direct consequence of the fact that the reservoirs are at thermal equilibrium, and (2) the convexity of the entropy production.

Many things are omitted from this article. In particular we do not discuss at all the Kubo relations for computing transport coefficients, nor do we include recent work by the authors⁵ on the heat flow in harmonic crystals or recent results about the heat flow in a random harmonic chain.⁶ The reason is that we tried to cover the weak coupling situation as fully as possible at the moment.

II. THE MICROSCOPIC MODEL

We wish to describe steady-state nonequilibrium processes such as heat flow in a spatially confined system $\mathcal{S}$. To sustain a truly steady heat flow, diffusion, or chemical reactions throughout the system, we have to couple $\mathcal{S}$ to inexhaustible energy and particle reservoirs $\mathcal{R}$. In fact, we treat here only heat conduction, since the essential features of the problem appear already in this simplest case. Indeed, in the model we use, diffusion and chemical reactions would be treated in an analogous fashion and their inclusion would lead only to a "multiplication of indices" without giving any more physical insight. $\mathcal{R}$ is therefore chosen to be a collection of heat reservoirs at various temperatures.

Microscopically, the system $\mathcal{S}$ is described in the usual way. We associate with $\mathcal{S}$ a Hilbert space $\mathcal{H}$. The states of $\mathcal{S}$ are described by statistical operators or density matrices, which are positive operators on $\mathcal{H}$ normalized to trace one. Observables are self-adjoint operators on $\mathcal{H}$. The dynamics of the isolated system is governed by the unitary group $\exp(-iHt)$ generated by the Hamiltonian H . Since we want $\mathcal{S}$ to be a thermodynamically stable system, we have to assume that $Z = \text{tr}(\exp(-\beta H))$ exists for all positive β . H must therefore have a purely discrete spectrum, which is bounded below and has no finite limit points; that is, there are only a finite number of energy levels in any finite interval ΔE .

An inexhaustible heat reservoir will be modeled microscopically here by an infinitely extended quantum mechanical system with certain additional

structures. The necessity of an infinitely extended system can be seen from simple energy arguments: A finite reservoir can supply heat to (or extract heat from) the system only over a certain period of time. On a more precise level, we will later see that, in the "Markovian approximation," the influence of the reservoir on the system manifests itself through certain time correlation functions of the reservoir. To have an approach to stationarity it is necessary that these correlation functions decay faster than $1/t$. Such a decay is impossible for finite quantum systems, where because of the discreteness of the energy spectrum all correlation functions are almost periodic functions of t . Of course, if $\mathcal{R}$ is a very large quantum system, the correlation functions can be expected to have in general the right decay properties over long time spans. This expresses simply the fact that a large bucket of water "acts" for some purposes as a good heat reservoir. But clearly a piece of metal placed between two isolated buckets of water (or champagne) at different temperatures will never approach a truly stationary state in which heat is flowing through the metal bar (our system $\mathcal{S}$). It is therefore sensible to go over to the idealization of making $\mathcal{R}$ an infinitely extended system for which the faster than $1/t$ decay is expected to be true in general (and can be proved for certain simple systems like ideal gases).

The reservoir $\mathcal{R}$ is composed of r independent parts $\mathcal{R}^1, \dots, \mathcal{R}^r$, corresponding to heat baths with different temperatures. With each one of them we associate a Hilbert space $\mathcal{H}_k^R$, a time evolution $\exp(-iH_k^R t)$, and an equilibrium state (density matrix) ω^k for the temperature β_k^{-1} . Then the Hilbert space of the reservoir is the product $\mathcal{H}^R = \mathcal{H}_1^R \otimes \dots \otimes \mathcal{H}_r^R$. Since the various parts of the reservoir are isolated from each other the Hamiltonian H^R of $\mathcal{R}$ is the sum

$$H^R = H_1^R + \dots + H_r^R \quad (\text{II.1})$$

and the state of $\mathcal{R}$ with the k th part at temperature β_k^{-1} is

$$\omega^R = \omega^1 \otimes \dots \otimes \omega^r \quad (\text{II.2})$$

[The thoughtful reader might wonder how we incorporated the fact that the reservoir is infinitely extended and how we can define a Hamiltonian for a system with infinite energy. The reservoir enters in the description of the open system $\mathcal{S}$ only through certain time correlation functions $\langle A(t)B \rangle$. They are defined as the limit of the finite volume correlation functions $\langle A(t)B \rangle_V \rightarrow \langle A(t)B \rangle$ as $V \rightarrow \infty$, where $\langle \rangle_V$ denotes the average over the grand canonical ensemble. The crucial point is that we can always find a Hamiltonian H and a density matrix ω such that $\langle A(t)B \rangle = \text{tr}(\exp(iHt)A \exp(-iHt)B\omega)$. Of course, since H and ω are defined indirectly only through the limiting process $V \rightarrow \infty$, they will not have the

form familiar from the finite system (e.g., H usually has the whole real line as continuous spectrum and an eigenvalue zero). See Refs. 7, 8.]

We couple $\mathcal{S}$ and $\mathcal{R}$ by some bounded interaction operator λH^{SR} , where $\lambda \geq 0$ is the coupling strength. Then the self-adjoint Hamiltonian of the coupled system $\mathcal{S} + \mathcal{R}$ is given by

$$H_\lambda = H \otimes 1^R + 1 \otimes H^R + \lambda H^{SR} \quad (\text{II.3})$$

acting on the Hilbert space $\mathcal{H} \otimes \mathcal{H}^R$. The time evolution of the statistical operator W is given by

$$U_t^\lambda W = \exp(-iH_\lambda t) W \exp(iH_\lambda t) \quad (\text{II.4})$$

It is convenient to think of U_t^λ as acting in the space of all density matrices, that is, in the so-called trace class $T(\mathcal{H} \otimes \mathcal{H}^R)$. (This is the space of all operators on $\mathcal{H} \otimes \mathcal{H}^R$ such that $\text{tr} |W| < \infty$. It is a Banach space under the norm $\|W\|_1 = \text{tr} |W|$.)

The reservoir by itself is of no interest to us. It forms merely a convenient microscopic device to induce steady flows throughout the system. Therefore we derive, following well-known methods,⁹⁻¹⁸ a generalized master equation describing the reduced dynamics of the system. We assume that the initial state of $\mathcal{S} + \mathcal{R}$ is uncorrelated and of the form $\rho \otimes \omega^R$, where ρ is an arbitrary density matrix of $\mathcal{S}$. Then, in the Schrödinger picture, the reduced dynamics Λ_t^λ of the system is defined by taking the partial trace over all degrees of freedom of the reservoir

$$\Lambda_t^\lambda \rho = \text{tr}_R [U_t^\lambda (\rho \otimes \omega^R)] \quad (\text{II.5})$$

Λ_t^λ describes the time evolution of $\mathcal{S}$ coupled to the reservoirs. To derive the master equation, one thinks of (II.5) as a projection on $T(\mathcal{H} \otimes \mathcal{H}^R)$. Let us define an amplification $\mathcal{A}: T(\mathcal{H}) \rightarrow T(\mathcal{H} \otimes \mathcal{H}^R)$ by

$$\mathcal{A}\rho = \rho \otimes \omega^R \quad (\text{II.6})$$

Then

$$P = \mathcal{A} \text{tr}_R \quad (\text{II.7})$$

projects $T(\mathcal{H} \otimes \mathcal{H}^R)$ to the subspace $T(\mathcal{H}) \otimes \omega^R$. We can now write (II.5) as $(\Lambda_t^\lambda \rho) \otimes \omega^R = P U_t^\lambda (\rho \otimes \omega^R)$. Let V_t^λ be the time evolution on $T(\mathcal{H} \otimes \mathcal{H}^R)$ generated by $P[H_\lambda, \cdot]P + (1-P)[H_\lambda, \cdot](1-P)$ and let us assume $\text{tr}_R \omega^R H^{SR} = 0$. We consider U_t^λ as a perturbation of V_t^λ . Then, by a well-known formula (which can be verified directly by differentiation),

$$U_t^\lambda = V_t^\lambda - i\lambda \int_0^t ds V_{t-s}^\lambda (P[H^{SR}, \cdot](1-P) + (1-P)[H^{SR}, \cdot]P) U_s^\lambda \quad (\text{II.8})$$

Projecting on the right and on the left, we obtain

$$PU_t^\lambda P = V_t^\lambda P - i\lambda \int_0^t ds V_{t-s}^\lambda P[H^{SR}, \cdot](1-P)U_s^\lambda P \quad (\text{II.9})$$

and

$$(1-P)U_t^\lambda P = -i\lambda \int_0^t ds V_{t-s}^\lambda (1-P)[H^{SR}, \cdot]PU_s^\lambda P \quad (\text{II.10})$$

and by substituting (II.10) into (II.9)

$$\begin{aligned} PU_t^\lambda P &= V_t^\lambda P + \lambda^2 \int_0^t ds \int_0^s du V_{t-s}^\lambda P[H^{SR}, \cdot](1-P) \\ &\quad \times V_{s-u}^\lambda (1-P)[H^{SR}, \cdot]PU_u^\lambda P \end{aligned} \quad (\text{II.11})$$

If we identify $PT(\mathcal{H} \otimes \mathcal{H}^R) = T(\mathcal{H}) \otimes \omega^R$ with $T(\mathcal{H})$, then (II.11) can be written as

$$\Lambda_t^\lambda \rho = \Lambda_t^0 \rho + \lambda^2 \int_0^t ds \int_0^s du \Lambda_{t-s}^0 K^\lambda(s-u) \Lambda_u^\lambda \rho \quad (\text{II.12})$$

which is the desired integral equation for the reduced dynamics. On differentiating, we obtain the generalized master equation of Nakajima, Prigogine, Résibois, and Zwanzig:¹⁰⁻¹²

$$\frac{d}{dt} \rho(t) = -i[H, \rho(t)] + \lambda^2 \int_0^t ds K^\lambda(t-s) \rho(s) \quad (\text{II.13})$$

The integral kernel $K^\lambda(s)$ is given by

$$K^\lambda(s) = -\text{tr}_R ([H^{SR}, \cdot](1-P)V_s^\lambda(1-P)[H^{SR}, \cdot]\mathcal{A}) \quad (\text{II.14})$$

$K^\lambda(s)$ admits a power series expansion in the coupling constant λ given by

$$K^\lambda(s) = \Lambda_s^0 \left[K_0(s) + \sum_{n=1}^{\infty} (-i)^n \lambda^n \int_{0 \leq t_1 \leq \dots \leq t_n \leq s} dt_n \dots dt_1 K_n(s, t_n, \dots, t_1) \right] \quad (\text{II.15})$$

where

$$K_0(s) = -\text{tr}_R ([H^{SR}(s), \cdot](1-P)[H^{SR}, \cdot]\mathcal{A}) \quad (\text{II.16})$$

$$\begin{aligned} K_n(s, t_n, \dots, t_1) &= \text{tr}_R ([H^{SR}(s), \cdot](1-P)[H^{SR}(t_n), \cdot](1-P) \\ &\quad \dots (1-P)[H^{SR}(t_1), \cdot](1-P)[H^{SR}, \cdot]\mathcal{A}) \end{aligned} \quad (\text{II.17})$$

and

$$[H^{SR}(t), \cdot] = U_{-t}^0 [H^{SR}, \cdot] U_t^0 = [\exp(iH_0 t) H^{SR} \exp(-iH_0 t), \cdot] \quad (\text{II.18})$$

If we choose for H^{SR} a linear coupling of the form $V \otimes V^R$ (or a sum of such linear couplings), then $K_n(s, t_n, \dots, t_1)$ depends on the (equilibrium) multitime correlation functions $\text{tr}_R(\omega^R V^R(t'_n) \dots V^R(t'_1) V^R)$ with $V^R(t) = \exp(iH^R t) V^R \exp(-iH^R t)$.

The first step in studying nonequilibrium steady state properties of $\mathcal{S}$ is to obtain the stationary state ρ_{st}^λ . If the reservoir temperatures are not too far apart and if H^{SR} represents a "good coupling," it seems safe to assume that there exists a unique stationary state ρ_{st}^λ and that every initial state approaches this state as $t \rightarrow \infty$. Therefore we should define

$$\rho_{st}^\lambda = \lim_{t \rightarrow \infty} \Lambda_t^\lambda \rho \quad (\text{II.19})$$

Unfortunately, our knowledge about the existence of this limit is—at the present rather poor, which should come as no surprise, since (II.19) is related to establishing mixing (which is a stronger notion than ergodicity) for the infinite system $\mathcal{S} + \mathcal{R}$. Only in the case where $\mathcal{S} + \mathcal{R}$ together form either an infinite ideal solid (harmonic crystal) or an infinite ideal gas (or some other quasifree system) the existence of the limit (II.19) has been proved.^{19–28} Of course, we are happy to admit any simplification on parts of the reservoir. But the system $\mathcal{S}$ should be something like a real physical system and the border cases ideal solid and ideal gas are of very limited interest; even worse, Fourier's law is not obeyed in such systems. They have an infinite thermal conductivity.^{29,30} (This should be contrasted with the fact that an ideal gas obeys the laws of equilibrium thermodynamics.)

In view of this situation we look for a simplification of (II.13). If λ becomes small we might neglect all higher-order terms in (II.15). A further simplification is obtained if the memory terms present in $K_0(s)$ become negligible. From the structure of the integral kernel $K_0(s)$ we expect such a situation if the time scale on which $\rho(t)$ varies is much longer than the decay time of the kernel $K_0(s)$, that is, than the decay time of the correlation functions of the reservoir appearing in (II.16). For small λ and large t we then obtain the Born approximation to the master equation (II.13) as

$$\frac{d}{dt} \rho = -i[H, \rho] + \left(\lambda^2 \int_0^\infty ds K(s) \right) \rho \quad (\text{II.20})$$

which is the generalized Pauli equation. The original Pauli equation considered only transitions between energy eigenstates. Equation II.20 is a Markovian evolution equation on the whole space $T(\mathcal{H})$ of statistical operators. A precise definition of this weak coupling limit involves two points. First, we have to go from the Schrödinger picture to the interaction picture in order to suppress oscillations of parts of the system that happen

to be uncoupled. Second, to make up for the slowing of the decay as $\lambda \rightarrow 0$, we have to rescale the physical time t in such a way that $\lambda^2 t = \tau$ is kept fixed. This is the van Hove limit^{31,32} that has been made rigorous under some conditions by Davies. The theorem of Davies, to be discussed in the next section, asserts the existence of

$$\lim_{\lambda \rightarrow 0} \Lambda_{-\lambda^{-2}\tau}^0 \Lambda_{\lambda^{-2}\tau}^\lambda \rho = e^{L\tau} \rho \quad (\text{II.21})$$

which is, roughly, the integrated form of (II.20). L is a linear operator on $T(\mathcal{H})$.

All our microscopic treatment of the thermodynamics of irreversible processes is in terms of the time evolution $\{e^{L\tau} | \tau \geq 0\}$ of $\mathcal{S}$ obtained in the weak coupling limit. It is therefore essential to discuss at this point precisely what information about the irreversible processes is preserved in the weak coupling limit. After all, we work in the interaction picture, we let $\lambda \rightarrow 0$ and the physical time $t \rightarrow \infty$, and a priori it is unclear whether these limits just destroy all that we are interested in.

The coupling of a real physical system to a heat reservoir is always at the surface via short-range forces. The interaction energy H^{SR} should therefore be roughly proportional to the surface, that is, should be small compared to the bulk energy H . This crude argument gives some hope that at least some relevant information is preserved in the weak coupling limit.

To get a somewhat more precise idea, let us assume that the limit (III.19) exists and is unique. Furthermore, let $\{e^{L\tau} | \tau \geq 0\}$ have a unique stationary state ρ_{st} ,

$$e^{L\tau} \rho_{st} = \rho_{st} \quad (\text{II.22})$$

for all $\tau \geq 0$. Then we expect that

$$\lim_{\lambda \rightarrow 0} \rho_{st}^\lambda = \rho_{st} \quad (\text{II.23})$$

The limit $t \rightarrow \infty$ does not enter, since we look at a sequence of stationary states. The interaction picture drops out, since, as we show later, the stationary state obtained in the weak coupling limit is invariant under the isolated time evolution, which means that ρ_{st} commutes with H . Thus in the weak coupling limit we should obtain the lowest (zeroth) order contribution in λ to the stationary state ρ_{st}^λ , that is, $\rho_{st}^\lambda = \rho_0 + \lambda \rho_1 + \dots$ with $\rho_0 = \rho_{st}$. In the case of a single reservoir temperature β^{-1} , ρ_0 is just the canonical ensemble $Z^{-1} \exp(-\beta H)$.

Since ρ_0 commutes with H , ρ_0 does not describe the local heat flow inside the system. This phenomenon would be described by the first-order contribution ρ_1 , which cannot be obtained by the methods of the weak

coupling limit. However, we can still compute the total amount of energy flowing through the system to lowest (λ^2) order in λ . Let us assume that the reservoir consists of a left part $\mathcal{R}^l$ and a right part $\mathcal{R}^r$ at different temperatures. The steady-state heat flow $\langle J \rangle_\lambda$ can be defined as the change of energy of $\mathcal{S}$ due to the coupling to the left heat reservoir averaged over the stationary state

$$\langle J \rangle_\lambda = \left\langle \left(\frac{d}{dt} H(t) \right)_{\text{left}} \right\rangle_\lambda \quad (\text{II.24})$$

where $\langle \cdot \rangle_\lambda$ denotes the average over the stationary state of $\mathcal{S} + \mathcal{R}$ and $(\cdot)_{\text{left}}$ denotes the time evolution coming from the coupling to the left reservoir. (The Hamiltonian generating this time evolution is given by $H \otimes 1 + 1 \otimes H_l^R + \lambda H_l^{SR}$.) As $\lambda \rightarrow 0$, but $\lambda^2 t = \tau$ fixed, we should have the convergence

$$\langle (H(t))_{\text{left}} \rangle_\lambda \rightarrow \text{tr} (\rho_{st} (H(\tau))_{\text{left}}) = \text{tr} (\rho_{st} \exp(L_{\text{left}}^* \tau)(H)) \quad (\text{II.25})$$

The interaction picture has again been "absorbed" by the invariance of ρ_{st} under the isolated time evolution of $\mathcal{S}$. If we assume that also the derivatives converge

$$\frac{1}{\lambda^2} \langle J \rangle_\lambda = \frac{1}{\lambda^2} \left\langle \left(\frac{d}{dt} H(t) \right)_{\text{left}} \right\rangle_\lambda \rightarrow \text{tr} \left(\rho_{st} \left(\frac{d}{d\tau} H(\tau) \right)_{\text{left}} \right) = \text{tr} (\rho_{st} L_{\text{left}}^* (H)) = \langle J \rangle \quad (\text{II.26})$$

then it follows that the lowest-order contribution to the average heat flow is of order λ^2 and that $\lambda^{-2} \langle J \rangle_\lambda$ converges to a quantity $\langle J \rangle$, which is defined in Section V as the heat flow in the weak coupling limit.

Of course, these are plausibility arguments only. Their proof would require as prerequisite the proof of the existence of the limit (II.19). We investigated⁵ these questions at a model system, where $\mathcal{S}$ is a classical harmonic chain of N particles (arbitrary couplings and masses) and $\mathcal{R}$ consists of two semi-infinite harmonic chains of equal masses ($=1$) and nearest neighbor coupling of unit strength coupled to the first and the N th particle of $\mathcal{S}$. The conditions on "good coupling" are that all eigenfrequencies ω of $\mathcal{S}$ are in the range $0 < \omega < 2$ and that the sum of the first and N th component of every eigenmode does not vanish. If they are fulfilled, then one can prove the existence of the limits (II.19) to (II.26) and the interchange of the various limits involved.

Let us summarize: We consider a spatially confined quantum mechanical system $\mathcal{S}$ coupled to inexhaustible heat reservoirs at various temperatures. We perform the weak coupling limit and obtain a Markovian time evolution for the system $\mathcal{S}$. We study irreversible processes in $\mathcal{S}$ in terms of this

time evolution. Then, as long as we consider a steady-state situation, we obtain results that are valid to the lowest nonvanishing order in the coupling constant λ .

III. THE WEAK COUPLING LIMIT

We investigate in more detail under what conditions the weak coupling limit (II.21) of the generalized master equation (II.12) exists and study some of its properties. We follow with minor extensions (see Ref. 33) the work of Davies.¹⁸ References 34 and 35 contain an extension of the theory developed in Ref. 18. A study of the weak coupling limit for specific model systems can be found in Refs. 36 to 39 and in Ref. 5. A rigorous model close to van Hove's original considerations can be found in Ref. 40. Readers interested in the various physical applications of the van Hove or weak coupling limit are referred to the review articles.^{15,16} Starting with (II.12), we rescale the time $\lambda^2 t = \tau$ and go over to the interaction picture

$$\begin{aligned} & \Lambda_{-\lambda}^0 \Lambda_{-\lambda}^{-2\tau} \Lambda_{\lambda}^{\lambda-2\tau} \rho \\ &= \rho + \int_0^\tau d\sigma \left\{ \Lambda_{-\lambda}^0 \Lambda_{-\lambda}^{-2\sigma} \left[\int_0^{\lambda^{-2}(\tau-\sigma)} dx \Lambda_{-\lambda}^0 K^\lambda(x) \right] \Lambda_{\lambda}^0 \Lambda_{-\lambda}^{-2\sigma} \right\} \Lambda_{-\lambda}^0 \Lambda_{-\lambda}^{-2\sigma} \Lambda_{\lambda}^{\lambda-2\sigma} \rho \end{aligned} \quad (\text{III.1})$$

where ρ is the density matrix of the system at time $t = 0$. We recall that Λ_t^0 is simply the uncoupled time evolution of the system, which does not depend on λ , $\Lambda_t^0 \rho = e^{-iHt} \rho e^{iHt}$. Expanding K^λ as in (II.15), we expect that in the limit as $\lambda \rightarrow 0$ only the K_0 term will contribute. The integration up to $\lambda^{-2}(\tau-\sigma)$ extends to infinity as $\lambda \rightarrow 0$. Therefore, with $\rho(\tau) = \lim_{\lambda \rightarrow 0} \Lambda_{-\lambda}^0 \Lambda_{-\lambda}^{-2\tau} \Lambda_{\lambda}^{\lambda-2\tau} \rho$,

$$\rho(\tau) = \rho(0) + \lim_{\lambda \rightarrow 0} \int_0^\tau d\sigma \Lambda_{-\lambda}^0 \Lambda_{-\lambda}^{-2\sigma} K \Lambda_{\lambda}^0 \Lambda_{-\lambda}^{-2\sigma} \rho(\sigma) \quad (\text{III.2})$$

where

$$K = \int_0^\infty dx K_0(x) \quad (\text{III.3})$$

The remaining limit is an averaging of K with respect to the free time evolution Λ_t^0 . Since the spectrum of H is purely discrete, this time average always exists and is given by

$$L = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T dt \Lambda_{-t}^0 K \Lambda_t^0 = \sum_{\omega \in \text{Sp}(H, \cdot)} Q_\omega K Q_\omega \quad (\text{III.4})$$

Here Q_ω are the spectral projections of $[H, \cdot]$ considered as an operator on

the trace class $T(\mathcal{H})$ corresponding to the eigenvalue ω , i.e.,

$$Q_\omega \rho = \sum_{\varepsilon_m - \varepsilon_n = \omega} P_m \rho P_n$$

where

$$H = \sum_i \varepsilon_i P_i \quad (\text{III.5})$$

is the spectral representation of the Hamiltonian H . Since H^{SR} was assumed to be bounded, K and L are bounded operators on the Banach space $T(\mathcal{H})$. Inserting (III.4) in (III.2), we obtain

$$\rho(\tau) = \rho(0) + \int_0^\tau d\sigma L\rho(\sigma) \quad (\text{III.6})$$

or, equivalently,

$$\frac{d}{d\tau} \rho(\tau) = L\rho(\tau), \quad \rho(\tau) = e^{L\tau} \rho = \Lambda_\tau \rho \quad (\text{III.7})$$

which is the desired Markovian limit of (II.13).

Davies proves that with suitable bounds on the K_n 's, our heuristic argumentation is indeed valid.

Theorem 1 (Davies). Let

$$\int_0^\infty dt \|K_0(t)\| < \infty \quad (\text{III.8})$$

$$\int_{0 \leq t_1 \leq \dots \leq t_n \leq t} dt_n \dots dt_1 \|K_n(t, t_n, \dots, t_1)\| \leq a_n(t)$$

and let the $a_n(t)$ be bounded by

$$a_n(t) \leq c_n t^{n/2} \quad (\text{III.9})$$

for all $t \geq 0$, where $\sum_{n=1}^\infty c_n z^n$ has an infinite radius of convergence, and by

$$a_n(t) \leq d_n t^{n/2-\varepsilon} \quad (\text{III.10})$$

for some $\varepsilon > 0$, $d_n \geq 0$, and all $t \geq 0$. Then in the norm topology of $T(\mathcal{H})$

$$\lim_{\lambda \rightarrow 0} \|\Lambda_{-\lambda}^{-0-2\tau} \Lambda_\lambda^{0-2\tau} \rho - e^{L\tau} \rho\|_1 = 0 \quad (\text{III.11})$$

for all $\rho \in T(\mathcal{H})$ uniformly on every finite interval $[0, \tau_0]$.

If the reservoir is quasifree (e.g., an ideal gas), then all higher-order correlation functions are expressible as sums of two-point correlation functions. As Davies shows, the conditions (III.8) and (III.10) reduce then

(at least for a quasifree Fermi system) to a single condition on the two-point function. If H^{SR} is of the form $V \otimes V^R$, then the bound

$$|\mathrm{tr}_R(\omega_R V^R(t) V^R)| \leq a(1+t)^{-(1+\varepsilon)} \quad (\text{III.12})$$

for some $\varepsilon > 0$ and all $t \geq 0$ is sufficient for the theorem to hold. Equation III.12 means that the time-dependent correlation function of V^R evolving under the isolated reservoir time evolution decays faster than t^{-1} . (See Ref. 41 for an extension to reservoirs that are not quasifree.)

For our further investigations we need a more explicit form of the generator L . First, we treat the case of a single reservoir at temperature β^{-1} . We assume that the interaction operator H^{SR} has the form

$$H^{SR} = \sum_{\alpha} V_{\alpha} \otimes V_{\alpha}^R \quad (\text{III.13})$$

where $V_{\alpha} = V_{\alpha} \in B(\mathcal{H})$, $V_{\alpha}^R = V_{\alpha}^R \in B(\mathcal{H}^R)$, $\sum_{\alpha} \|V_{\alpha}\|^2 < \infty$, and, as before, $\mathrm{tr}_R(\omega^R V_{\alpha}^R) = 0$. $B(\mathcal{H})$ denotes all bounded operators on $\mathcal{H}$. Since K contains the correlation functions $\mathrm{tr}_R(\omega^R V_{\gamma}^R V_{\alpha}^R(t))$ and since L is the time average of K , the Fourier transforms

$$h_{\alpha\gamma}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \mathrm{tr}_R(\omega^R V_{\gamma}^R V_{\alpha}^R(t)) \quad (\text{III.14})$$

will enter the generator L . We now exploit the fact that ω^R is a thermal equilibrium state to derive an important relation for $h_{\alpha\gamma}$. Thermal equilibrium states of both finite and infinite quantum systems are defined by the Kubo–Martin–Schwinger (KMS) boundary condition.^{42,43} We call a state, defined by the density matrix W , a KMS state (thermal equilibrium state) for inverse temperature β if

$$\mathrm{tr}(WAB(t)) = \mathrm{tr}(WB(t-i\beta)A) \quad (\text{III.15})$$

for all observables A, B , and all t . As usual $B(t-i\beta)$ is defined as $\exp(i(t-i\beta)H)B \exp(-i(t-i\beta)H)$, where H is the Hamiltonian of the system under consideration. (We disregard domain questions that can be handled, however.) The reader may check that for a system in a box, (III.15) admits as only solution $e^{-\beta H}/Z(\beta)$. If the system is infinitely extended, there might be (and in some cases definitely is) more than one solution of (III.15) indicating the existence of phase transitions.

Using the KMS boundary condition (III.15) for ω^R and, as a direct consequence, the time invariance of ω^R , we obtain

$$\begin{aligned} h_{\alpha\gamma}(\omega) &= e^{\beta\omega} \int_{-\infty}^{\infty} dt e^{-i\omega t} \mathrm{tr}_R(\omega^R V_{\alpha}^R(t) V_{\gamma}^R) \\ &= e^{\beta\omega} \int_{-\infty}^{\infty} dt e^{i\omega t} \mathrm{tr}_R(\omega^R V_{\alpha}^R V_{\gamma}^R(t)) = h_{\gamma\alpha}(-\omega) e^{\beta\omega} \end{aligned} \quad (\text{III.16})$$

that is,

$$h_{\gamma\alpha}(-\omega) = e^{-\beta\omega} h_{\alpha\gamma}(\omega)$$

Since $\{h_{\alpha\gamma}(\omega)\}$ is the Fourier transform of time-dependent correlation functions, it is a positive matrix for all ω . Equation III.16 is essential for deriving the Onsager relations, the principle of minimal entropy production, and other basic postulates of thermodynamics of irreversible processes. To state it in a somewhat oversimplified way: In our model irreversible thermodynamics follows from the fact that the reservoirs are at thermal equilibrium.

We define the Hilbert transform $s_{\alpha\gamma}$ of $h_{\alpha\gamma}$ as

$$\begin{aligned} s_{\alpha\gamma}(\omega) &= i \int_0^\infty dt e^{-i\omega t} \text{tr}_R (\omega^R V_\gamma^R V_\alpha^R(t)) - \frac{1}{2} h_{\alpha\gamma}(\omega) \\ &= \frac{1}{2\pi} \mathcal{P} \int_{-\infty}^\infty \frac{h_{\alpha\gamma}(\lambda)}{\lambda - \omega} d\lambda \end{aligned} \quad (\text{III.17})$$

where $\mathcal{P}$ denotes the principal part, and introduce the operators

$$V_\alpha(\omega) = \sum_{\varepsilon_m - \varepsilon_n = \omega} P_n V_\alpha P_m = V_\alpha(-\omega) \quad (\text{III.18})$$

If we now perform for the chosen H^{SR} the integration (III.3) and the average (III.4), we obtain for the generator $L: T(\mathcal{H}) \rightarrow T(\mathcal{H})$

$$\begin{aligned} L(\rho) &= \sum_{\omega \in \text{Sp}([H, \cdot])} \sum_{\alpha\gamma} \{-is_{\alpha\gamma}(\omega)[V_\gamma(\omega)^* V_\alpha(\omega), \rho] \\ &\quad + h_{\alpha\gamma}(\omega)([V_\alpha(\omega)\rho, V_\gamma(\omega)^*] + [V_\alpha(\omega), \rho V_\gamma(\omega)^*])\} \end{aligned} \quad (\text{III.19})$$

$\text{Sp}([H, \cdot])$ denotes the spectrum of the Liouville-von Neumann operator $[H, \cdot]$. It is the set $\{\varepsilon_m - \varepsilon_n | \varepsilon_m, \varepsilon_n \in \text{Sp}(H)\}$. The generator L is the sum of a Hamiltonian part L_a (the $s_{\alpha\gamma}$ -term) and a dissipative part L_s (the $h_{\alpha\gamma}$ -term). Here $e^{Lt}\rho$ describes the time evolution of states (Schrödinger picture). As in the quantum mechanics of isolated systems, one is often interested in the time evolution of observables A (Heisenberg picture), which is clearly to be defined by

$$\begin{aligned} \text{tr}(A e^{Lt}(\rho)) &= \text{tr}(e^{L^*t}(A)\rho) \\ \text{tr}(AL(\rho)) &= \text{tr}(L^*(A)\rho) \end{aligned} \quad (\text{III.20})$$

The dual L^* of L is defined by (III.20) and acts now on observables. With the help of (III.19) and (III.20) we find

$$\begin{aligned} L^*(A) &= \sum_{\omega \in \text{Sp}([H, \cdot])} \sum_{\alpha\gamma} \{is_{\alpha\gamma}(\omega)[V_\gamma(\omega)^* V_\alpha(\omega), A] \\ &\quad + h_{\alpha\beta}(\omega)([V_\gamma^*(\omega), A] V_\alpha(\omega) + V_\gamma^*(\omega)[A, V_\alpha(\omega)])\} \end{aligned} \quad (\text{III.21})$$

Three points should be noted: (1) The reservoir temperature enters via $h_{\alpha\gamma}$ through the KMS condition (III.16). (2) The "reservoir part" of the interaction H^{SR} is reflected by the numerical coefficients $h_{\alpha\gamma}$ and $s_{\alpha\gamma}$, the "system part" of H^{SR} by the $V_\alpha(\omega)$'s. (3) The Hamiltonian H of $\mathcal{S}$ enters indirectly through the $V_\alpha(\omega)$'s by definition (III.18).

We list a few properties of the generator L :

Property 1. The canonical ensemble $\rho_\beta = Z^{-1} e^{-\beta H}$ is stationary,

$$L(\rho_\beta) = 0, \quad e^{Lt} \rho_\beta = \rho_\beta \quad (\text{III.22})$$

for all $t \geq 0$. To prove (III.22), we insert ρ_β in (III.19) and use (III.16). In general, ρ_β is the only stationary state of $\{\Lambda_t | t \geq 0\}$ and every initial state approaches ρ_β as $t \rightarrow \infty$ (see Section VI, Theorem 3).

Property 2. Λ_t commutes with the free time evolution Λ_t^0 ,

$$e^{Lt} (e^{-iHt} \rho e^{iHt}) = e^{-iHt} (e^{Lt} \rho) e^{iHt} \quad (\text{III.23})$$

In particular, all functions of the energy in $T(\mathcal{K})$ form an invariant subspace for $\{\Lambda_t | t \geq 0\}$. Equation III.23 follows from the fact that L was defined as the time average over an operator K ; see (III.4).

Property 3. Let the spectrum of H be nondegenerate. Then, by property 2, statistical operators diagonal in the energy basis are transformed among themselves. If we denote the diagonal elements of a density matrix in the energy representation by p_j , they satisfy the Pauli master equation

$$\frac{d}{dt} p_j(t) = \sum_k (W_{jk} p_k(t) - W_{kj} p_j(t)) \quad (\text{III.24})$$

$p_j(t) \geq 0$, $\sum_j p_j(t) = 1$. The coefficients W_{jk} satisfy the detailed balance condition

$$W_{jk} e^{-\beta e_k} = W_{kj} e^{-\beta e_j} \geq 0 \quad (\text{III.25})$$

Equation III.25 is a consequence of (III.16). Since the spectrum of H is nondegenerate, the $s_{\alpha\gamma}$ -term of L vanishes. In the dissipative part L_s of L $2V_\alpha(\omega)\rho V_\gamma(\omega)^*$ gives the first term and $-V_\gamma(\omega)^* V_\alpha(\omega)\rho - \rho V_\gamma(\omega)^* V_\alpha(\omega)$ gives the second term in (III.24).

Property 4. The generator L satisfies the (quantum generalization of the) detailed balance condition with respect to ρ_β

$$L_a(\rho_\beta) = 0 \quad (\text{III.26})$$

$$L_s(A\rho_\beta) = L_s^*(A)\rho_\beta \quad (\text{III.27})$$

Equation III.26 is obvious; (III.27) requires some algebraic manipulations, where use is made of (III.16).

Let us define the scalar product $\langle A|B\rangle_\beta = \text{tr}[\rho_\beta AB^*]$ on $B(\mathcal{H})$. Then we can rewrite (III.26) and (III.27) as

$$\begin{aligned}\langle L_a^*(A)|B\rangle_\beta &= -\langle A|L_a^*(B)\rangle_\beta \\ \langle L_s^*(A)|B\rangle_\beta &= \langle A|L_s^*(B)\rangle_\beta\end{aligned}\quad (\text{III.28})$$

Therefore L_a^* is antisymmetric and L_s^* is symmetric with respect to the scalar product $\langle \cdot | \cdot \rangle_\beta$. Here (III.28) is the quantum generalization of the detailed balance (III.25) as proposed and studied by Alicki⁴⁴ and Kossakowski, Frigerio, Gorini, and Verri.⁴⁵ Equation III.28 is characteristic for a system weakly coupled to a single heat reservoir. If $\mathcal{S}$ is coupled in a nontrivial way to two reservoirs at different temperatures, detailed balance is not fulfilled.

Although at first sight the generator L has a rather complicated structure, properties 1 to 3 allow one to visualize the time evolution $\{e^{Lt}|t \geq 0\}$ fairly well. We expand $\rho(t) = e^{Lt}\rho$ in an energy basis. Then, generally, the off-diagonal elements $\langle n|\rho(t)|m\rangle$, $n \neq m$, decay exponentially, whereas the diagonal elements $\langle n|\rho(t)|n\rangle$, by transitions according to (III.24), finally reach their canonical equilibrium value. Certainly this picture has to be modified in some cases. If the spectrum of H is degenerate, then property 3 is no longer true. One may have then transitions between diagonal and off-diagonal elements. Clearly, also if the coupling is trivial, say $V_\alpha = 1$ for $\alpha = 1$ and $V_\alpha = 0$ otherwise, then $L = 0$ (since the weak coupling limit is obtained in the interaction picture). In Theorem 3 we give a criterion for what is the exception and what the rule.

Let $\mathcal{S}$ be coupled now to the heat reservoirs $\mathcal{R}^1, \dots, \mathcal{R}^r$ in equilibrium at inverse temperatures $\beta_1, \dots, \beta_r$. Since the reservoir parts are independent from each other, the generator L of the weak coupling limit (III.7) is the sum of the generators $L_1, \dots, L_r$

$$L = L_1 + \dots + L_r \quad (\text{III.29})$$

L_k generates the time evolution of $\mathcal{S}$ weakly coupled only to $\mathcal{R}^k$, $k = 1, \dots, r$. Each L_k has the form given in (III.19) with $h_{\alpha\gamma}^k(\omega)$ satisfying the KMS condition (III.16) with reciprocal temperature β_k .

IV. DETAILED BALANCE AND THE KMS CONDITION

In the preceding section we showed that for a system coupled to a single reservoir at temperature β^{-1} : KMS (of the reservoir) + weak coupling $\rightarrow$ detailed balance with respect to the canonical ensemble ρ_β (of the system). The importance of the detailed balance property derives from the fact that, as is seen later, together with the convexity of the entropy production, it implies essentially all postulates of thermodynamics of irreversible pro-

cesses. In this section we want to argue the converse: detailed balance of the system + weak coupling $\rightarrow$ KMS (of the reservoir), which may be viewed as a stability property^{46,47} that singles out the equilibrium states. This indicates the deep connection between detailed balance (and therefore irreversible thermodynamics) and the KMS boundary condition. The results of this section are due to Kossakowski, Frigerio, Gorini, and Verri,⁴⁵ where also the proofs may be found. (The notions used in this section are slightly more abstract than those used otherwise, and it may be omitted without preventing understanding of Sections V to VIII.)

To begin with, we abandon our particular microscopic model, retaining only the assumption that the time evolution of our open quantum-mechanical system $\mathcal{S}$ is Markovian. This leads us to the definition of a dynamical semigroup.⁴⁸ A dynamical semigroup is a one-parameter family of linear mappings

$$\Lambda_t: T(\mathcal{H}) \rightarrow T(\mathcal{H}), \quad t \geq 0 \quad (\text{IV.1})$$

which are positive, $\rho \geq 0$ implies $\Lambda_t \rho \geq 0$, are trace-preserving, $\text{tr}(\Lambda_t \rho) = \text{tr}(\rho)$ form a semigroup

$$\Lambda_{t+s} = \Lambda_t \Lambda_s \quad (\text{IV.2})$$

and are continuous in the trace norm,

$$\lim_{t \rightarrow 0_+} \|\Lambda_t \rho - \rho\|_1 = 0 \quad (\text{IV.3})$$

for all $\rho \in T(\mathcal{H})$. One can show that Λ_t is a contraction, $\|\Lambda_t\| = 1$. Positivity and preservation of the trace ensure that Λ_t maps density matrices on density matrices, (IV.2) is the Markovian property, and (IV.3) ensures, by the Hille–Yosida theorem,⁴⁹ the existence of a densely defined generator L such that $\Lambda_t = e^{Lt}$. In terms of the Heisenberg picture, defined by $\text{tr}(A \Lambda_t(\rho)) = \text{tr}(\Lambda_t^*(A) \rho)$ for all $\rho \in T(\mathcal{H})$, $A \in B(\mathcal{H})$, we have the following properties:

- (i') $\Lambda_t^* B(\mathcal{H})_+ \subset B(\mathcal{H})_+$
- (ii) $\Lambda_t^*(1) = 1$
- (iii) $\Lambda_{t+s}^* = \Lambda_t^* \Lambda_s^*$
- (iv') $\Lambda_t^*(A) \rightarrow A$ ultraweakly when $t \rightarrow 0_+$
- (v) Λ_t^* is ultraweakly continuous

$B(\mathcal{H})_+$ denotes the positive elements in $B(\mathcal{H})$ and a sequence $A_n \in B(\mathcal{H})$ converges ultraweakly to $A \in B(\mathcal{H})$, if $\text{tr}(A_n \rho) \rightarrow \text{tr}(A \rho)$ for all $\rho \in T(\mathcal{H})$.

The reduced dynamics Λ_t^* [cf. (II.5)] has another important property, as first pointed out by Kraus⁵⁰ in the context of state changes caused by quantum measurements and subsequently used by several authors.^{51,52} To

state this property, we recall a definition. Let $\mathcal{A}$ and $\mathcal{B}$ be C^* -algebras, and denote by $M(n)$ (n integer ≥ 1) the algebra of $n \times n$ complex matrices. A linear map $\phi: \mathcal{A} \rightarrow \mathcal{B}$ is called n -positive, if the map

$$\begin{aligned} \phi_n: \mathcal{A} \otimes M(n) &\rightarrow \mathcal{B} \otimes M(n) \\ \phi_n(A \otimes M) &= \phi(A) \otimes M, \quad A \in \mathcal{A}, \quad M \in M(n) \end{aligned} \quad (\text{IV.4})$$

is positive (i.e., maps a positive operator to a positive operator). ϕ is called completely positive, if it is n -positive for all integers n . The reduced dynamics Λ_t^* is completely positive for all t , since it is the composition of a $*$ -automorphism and a conditional expectation. Therefore it seems physically well motivated to replace the positivity (i') by the stronger property

$$(i) \quad \Lambda_t^* \text{ is completely positive for all } t \geq 0$$

For technical reasons it is convenient to require the continuity property

$$(iv) \quad \lim_{t \rightarrow 0_+} \|\Lambda_t^* - 1\| = 0 \quad (\text{IV.5})$$

which is stronger than (iv'). The norm continuity of Λ_t^* implies the existence of a bounded, ultraweakly continuous generator $L^*: B(\mathcal{H}) \rightarrow B(\mathcal{H})$ of Λ_t^* .

A family of mappings $\Lambda_t^*: B(\mathcal{H}) \rightarrow B(\mathcal{H})$, $t \geq 0$, with properties (i) to (v) is called a quantum-dynamical semigroup. (Readers interested in the theory of quantum-dynamical semigroups are referred to the book by Davies⁵³ and the review article by Gorini et al.³³ The review article by Ingarden and Kossakowski⁵⁴ may serve as introduction.) Recently, Lindblad⁵¹ proved that the general form of the generator of a quantum-dynamical semigroup is given by

$$L^*(\mathcal{A}) = i[H, A] + \frac{1}{2} \sum_{j \in I} \{[V_j^*, A]V_j + V_j^*[A, V_j]\} \quad (\text{IV.6})$$

where H is a bounded self-adjoint operator, $V_j \in B(\mathcal{H})$ such that $\sum_{j \in I} V_j^* V_j$ converges ultraweakly, and the sum on the right-hand side converges ultraweakly. We note that the generator (III.21) obtained in the weak coupling limit is of the form (IV.6).

In analogy to (III.28) we define detailed balance for a quantum-dynamical semigroup.

Definition 1:

Let $\{\Lambda_t^* | t \geq 0\}$ be a quantum-dynamical semigroup with generator L^* . Let $\rho_0 \in T(\mathcal{H})$ be a density matrix with no zero eigenvalue and invariant under

Λ_t and let a product on $B(\mathcal{H})$ be defined by

$$\langle A|B\rangle_0 = \text{tr}(AB^*\rho_0) \quad (\text{IV.7})$$

Then $\{\Lambda_t^*|t \geq 0\}$ satisfies the detailed balance condition with respect to ρ_0 if L^* can be written as a sum

$$L^* = L_a^* + L_s^* \quad (\text{IV.8})$$

such that

$$L_a^* = i[H, \cdot] \text{ with } H \text{ self-adjoint and } [H, \rho_0] = 0$$

(then L_a^* is antisymmetric $\langle L_a^*(A)|B\rangle_0 = -\langle A|L_a^*(B)\rangle_0$)

$$L_s^* \text{ is symmetric, } \langle L_s^*(A)|B\rangle_0 = \langle A|L_s^*(B)\rangle_0$$

If Λ_t^* satisfies detailed balance with respect to ρ_0 and if the spectrum of ρ_0 is nondegenerate, then Λ_t induces on the states diagonal in the ρ_0 -basis a classical Markov process that satisfies the well-known detailed balance of the form (III.25). In this sense Definition 1 generalizes the classical case. The generators of quantum-dynamical semigroups satisfying the detailed balance condition have been completely classified.^{44,45}

Let us assume now that the reservoir $\mathcal{R}$ is in an arbitrary state ω^R invariant under the uncoupled time evolution. As long as Davies' conditions (III.8) to (III.10) are satisfied, we can perform the weak coupling limit and obtain again a semigroup with a generator of the form (III.21). However, h_{ij} will not satisfy (III.16), in general. Let us fix for a moment the reservoir part of the interaction $V_1^R = A$, $V_2^R = B$, $V_j^R = 0$, $j \neq 1, 2$, and let us denote h_{12} by h_{AB} . If we assume in addition that the semigroup obtained in the weak coupling limit satisfies the detailed balance condition with respect to some stationary ρ_0 , then this imposes certain restrictions on h_{AB} and on h_{BA} . If we assume detailed balance to be satisfied for a whole class of system Hamiltonians (in fact six-level systems suffice), then we obtain a whole class of restrictions on h_{AB} and on h_{BA} . The interesting point is that all these restrictions together admit only the single solution

$$h_{AB}(-\omega) = e^{-\beta\omega} h_{BA}(\omega) \quad (\text{IV.9})$$

for some β independent of A and B . By Fourier transformations we obtain the KMS condition (III.15) for A and B . We repeat the argument for other observables, for which Davies' conditions (Theorem 1) are satisfied. This shows then that ω^R has to be a KMS state on all these observables. Therefore if the state ω^R of the reservoir $\mathcal{R}$ is such that all systems weakly coupled to $\mathcal{R}$ in the state ω^R satisfy the detailed balance condition, then ω^R has to be a thermal equilibrium (KMS) state.

V. ENTROPY PRODUCTION

Entropy production plays a central role in nonequilibrium thermodynamics.^{55,56} The entropy production σ is the source term in the (local) balance equation for the entropy density

$$\frac{\partial S}{\partial t} = -\operatorname{div} \mathbf{J}_S + \sigma \quad (\text{V.1})$$

S being the local entropy density and $\mathbf{J}_S$ being the vector field of entropy flow per unit area per unit time. Here σ is assumed to be always non-negative, since entropy can only be created, never destroyed; for reversible processes $\sigma = 0$. This is the (local formulation) of the second law of thermodynamics. It turns out that in the phenomenological theory σ can be written as a bilinear form in the fluxes characterizing the irreversible process and in the conjugate thermodynamic forces. If only heat conduction can occur in the system, then the entropy production is given by

$$\sigma = -\frac{1}{T^2} \mathbf{J} \cdot (\operatorname{grad} T) \quad (\text{V.2})$$

where T is the temperature field and $\mathbf{J}$ is the vector field for the heat flow. (Here $\mathbf{J}$ is the flux and $-1/T^2 \operatorname{grad} T$ is the conjugate thermodynamic force.)

In our attempt to give a microscopic foundation to the thermodynamics or irreversible processes we should, therefore, in the first place, give a microscopic expression for the entropy production. To begin with, we treat the case of the system $\mathcal{S}$ weakly coupled to a reservoir at a single temperature β^{-1} . The time evolution of $\mathcal{S}$ is given by $\{e^{L_t}|t \geq 0\}$ in the weak coupling approximation (III.7). The entropy S of $\mathcal{S}$ in the state ρ is defined by the well-known expression of von Neumann

$$S(\rho) = -\operatorname{tr}(\rho \log \rho) \quad (\text{V.3})$$

The entropy flow is $-\beta dQ$ (Boltzmann's constant k is set equal to one), where dQ is the heat transfer from the reservoir to the system (i.e., dQ is the change of energy of S that occurs at a reservoir temperature β^{-1} and is reversible as far as the reservoir is concerned).

$$\begin{aligned} dQ &= \operatorname{tr}(\rho(t)L^*(H)) = \operatorname{tr}\left(\rho \frac{d}{dt} H(t)\right) \\ \mathbf{J}_S &= -\beta dQ = \frac{d}{dt} \operatorname{tr} \rho(t) \log \rho_\beta \end{aligned} \quad (\text{V.4})$$

where $\rho_\beta = Z^{-1} e^{-\beta H}$. Therefore, using the balance equation (V.1) in the

integrated form, we obtain for the (total) entropy production

$$\sigma(\rho) = \frac{d}{dt} (\text{tr}(\rho(t) \log \rho_\beta) - \text{tr}(\rho(t) \log \rho(t)))|_{t=0} \quad (\text{V.5})$$

$$\sigma(\rho) = -\frac{d}{dt} S(e^{L_t} \rho | \rho_\beta)|_{t=0} \quad (\text{V.6})$$

$S(\rho | \rho_\beta)$ is the relative entropy⁵⁷ of ρ with respect to ρ_β . Equation (V.6) is our basic definition.

Equation (V.5) is only a formal expression for the relative entropy, since both summands may be infinite. One way to define the relative entropy properly is

$$\begin{aligned} S(A|B) &= \sum_{i,j} |\langle a_i | b_j \rangle|^2 (a_i \log a_i - a_i \log b_j + b_j - a_i) \\ &= (\text{tr } A \log A - \text{tr } A \log B + \text{tr } B - \text{tr } A) \end{aligned} \quad (\text{V.7})$$

where A, B are statistical operators with eigenvalues $\{a_i\}, \{b_j\}$ and eigenvectors $\{|a_i\rangle\}, \{|b_j\rangle\}$. Since the second factor is nonnegative, $S(A|B) \geq 0$, possible $S(A|B) = \infty$. We note that $S(A|B) = \infty$, if the range of A is not contained in the range of B . (The range of A is the linear span of all eigenvectors to nonzero eigenvalues of A .)

We collect the essential properties of the entropy production in

Theorem 2. Let $\dim \mathcal{H} = N < \infty$ and let L be given by (III.19). Then the entropy production

$$\sigma(\rho) = -\frac{d}{dt} S(\rho | \rho_\beta)|_{t=0}$$

is given by

$$\begin{aligned} \sigma(\rho) &= \text{tr}(L(\rho)(\log \rho_\beta - \log \rho)) \\ &= \sum_{\omega \in \text{Sp}(H, \cdot)} \sum_{j,k=1}^N \left\{ \sum_{\alpha, \gamma} h_{\alpha\gamma}(\omega) \langle \Psi_j | V_\alpha(\omega) \Psi_k \rangle \langle \Psi_k | V_\gamma(\omega)^* \Psi_j \rangle \right\} \\ &\quad \times \{(\rho_k - \rho_j e^{-\beta\omega})(\log \rho_k - \log \rho_j + \beta\omega)\} \end{aligned} \quad (\text{V.8})$$

where $\rho = \sum_{j=1}^N \rho_j |\Psi_j\rangle \langle \Psi_j|$ is the spectral decomposition of ρ and where $\text{tr}(L(\rho) \log \rho)$ is defined by

$$\text{tr}(L(\rho) \log \rho) = \sum_{j=1}^N \langle \Psi_j | L(\rho) \Psi_j \rangle \log \rho_j \quad (\text{V.9})$$

$$\langle \Psi_j | L(\rho) \Psi_j \rangle \log \rho_j = \begin{cases} -\infty & \text{if } \langle \Psi_j | L(\rho) \Psi_j \rangle \neq 0 \text{ and } \rho_j = 0 \\ 0 & \text{if } \langle \Psi_j | L(\rho) \Psi_j \rangle = 0 \end{cases}$$

Here σ has the properties:

- (i) $\sigma(\rho) \geq 0$, possibly $\sigma(\rho) = \infty$. If $\{h_{\alpha\gamma}(\omega)\} > 0$ (as a matrix) for all $\omega \in \text{Sp}([H, \cdot])$, then $\sigma(\rho) = 0$ if and only if $L(\rho) = 0$.
(ii) σ is a convex function, that is,

$$\sigma(\lambda\rho_1 + (1-\lambda)\rho_2) \leq \lambda\sigma(\rho_1) + (1-\lambda)\sigma(\rho_2) \quad (\text{V.10})$$

$0 \leq \lambda \leq 1$, with statistical operators ρ_1, ρ_2 .

Proof: Since $\dim \mathcal{H} < \infty$ and since $\log \rho_\beta = -\beta H - Z$, we have

$$S(\rho(t)|\rho_\beta) = \text{tr}(\rho(t) \log \rho(t)) + \beta \text{tr}(\rho(t)H) + \beta Z \quad (\text{V.11})$$

The derivative of the second term is $\text{tr}(L(\rho) \log \rho_\beta)$. Using the spectral decomposition of $\rho(t)$, $\rho(t) = \sum_j \rho_j(t) |\Psi_j(t)\rangle \langle \Psi_j(t)|$, we obtain

$$\frac{d}{dt} \text{tr}(\rho(t) \log \rho(t))|_{t=0} = \sum_k \{ \rho_k \log \rho_k (\langle \dot{\Psi}_k(0) | \Psi_k \rangle + \langle \Psi_k | \dot{\Psi}_k(0) \rangle) + \dot{\rho}_k(0) \log \rho_k \} \quad (\text{V.12})$$

If $\rho_k = 0$ and $\dot{\rho}_k(0) > 0$, then $\dot{\rho}_k(0) \log \rho_k = -\infty$. If $\rho_k = 0$ and $\dot{\rho}_k(0) = 0$, then using a Taylor expansion of $\rho_k(t)$ ($\rho_k(t)$ is an analytic function) and performing the limit as $t \rightarrow 0_+$, one obtains $\dot{\rho}_k(0) \log \rho_k = 0$. Since

$$\langle \Psi_k | L(\rho) \Psi_k \rangle = \rho_k (\langle \dot{\Psi}_k(0) | \Psi_k \rangle + \langle \Psi_k | \dot{\Psi}_k(0) \rangle) + \dot{\rho}_k(0) \quad (\text{V.13})$$

we have

$$\frac{d}{dt} \text{tr}(\rho(t) \log \rho(t))|_{t=0} = \text{tr}(L(\rho) \log \rho) \quad (\text{V.14})$$

with the convention (V.9). We note that for $t > 0$, $\rho_k(t) = 0$ implies $\dot{\rho}_k(t) = 0$, since $\rho_k(t_-), \rho_k(t_+) \geq 0$.

We compute the entropy production $\sigma(\rho) = -\text{tr}(L(\rho) \log \rho) - \text{tr}(L(\rho) \beta H)$. We have $\text{tr}(L_\alpha(\rho) \log \rho) = 0$, since $[\rho, \log \rho] = 0$, and $\text{tr}(L_\alpha(\rho) H) = 0$, since $[H, V_\gamma^*(\omega) V_\alpha(\omega)] = 0$. The contribution of the symmetric part to the entropy production is

$$\begin{aligned} \sigma(\rho) &= 2 \sum_{\omega \in \text{Sp}([H, \cdot])} \sum_{j,k=1}^N \sum_{\alpha,\gamma} h_{\alpha\gamma}(\omega) \\ &\quad \times \langle \Psi_j | V_\alpha(\omega) \Psi_k \rangle \langle \Psi_k | V_\gamma(\omega) \Psi_j \rangle \rho_k (\log \rho_k - \log \rho_j + \beta \omega) \end{aligned} \quad (\text{V.15})$$

$$\begin{aligned} &= 2 \sum_{\omega \in \text{Sp}([H, \cdot])} \sum_{j,k=1}^N \sum_{\alpha,\gamma} h_{\alpha\gamma}(\omega) \\ &\quad \times \langle \Psi_j | V_\alpha(\omega) \Psi_k \rangle \langle \Psi_k | V_\beta(\omega) \Psi_j \rangle e^{-\beta \omega} \rho_j (\log \rho_j - \log \rho_k - \beta \omega) \end{aligned} \quad (\text{V.16})$$

where we used (III.16) and (III.18). Adding (V.15) and (V.16) and dividing by 2, one obtains (V.8).

From (V.8) it is obvious that $\sigma(\rho) \geq 0$. If $L(\rho) = 0$, then $\sigma(\rho) = 0$ by (V.8). Let $\sigma(\rho) = 0$. Since $\{h_{\alpha,\gamma}(\omega)\}$ is a positive matrix we can diagonalize it. Let $h_\gamma(\omega) \geq 0$ be its eigenvalues and let $\{\tilde{V}_\gamma(\omega)\}$ be $\{V_\alpha(\omega)\}$ expressed in the eigenbasis of $\{h_{\alpha,\gamma}(\omega)\}$. Then

$$\sigma(\rho) = \sum_{\omega \in \text{Sp}([H, \cdot])} \sum_{j,k=1}^N \sum_{\gamma} h_\gamma(\omega) |\langle \Psi_j | \tilde{V}_\gamma \Psi_k \rangle|^2 \times (\rho_k - \rho_j) e^{-\beta\omega} (\log \rho_k - \log \rho_j + \beta\omega) = 0 \quad (\text{V.17})$$

implies

$$h_\gamma(\omega) \langle \Psi_j | \tilde{V}_\gamma(\omega) \Psi_k \rangle (\rho_k - \rho_j e^{-\beta\omega}) = 0 \quad (\text{V.18})$$

for all $\gamma, \omega \in \text{Sp}([H, \cdot])$ and $j, k = 1, \dots, N$. Therefore

$$[\tilde{V}_\gamma(\omega), \rho e^{\beta H}] = 0 \quad (\text{V.19})$$

for all γ and $\omega \in \text{Sp}([H, \cdot])$. Let $\mathcal{N}$ be the set of all operators commuting with all $\tilde{V}_\gamma(\omega)$. Then

$$\rho = A e^{-\beta H} \quad (\text{V.20})$$

with $A \in \mathcal{N}$. We write the generator (III.19) in terms of the $\tilde{V}_\gamma(\omega)$. Then, since $A \in \mathcal{N}$,

$$[\tilde{V}_\gamma(\omega)^* \tilde{V}_\gamma(\omega), A e^{-\beta H}] = 0 \quad (\text{V.21})$$

which implies $L_\alpha(\rho) = 0$. By the detailed balance (III.27)

$$L_s(A e^{-\beta H}) = L_s^*(A) e^{-\beta H} = 0 \quad (\text{V.22})$$

since $A \in \mathcal{N}$. Therefore $L(\rho) = 0$.

To prove the convexity of σ we note that $\text{tr}(L(\rho) \log \rho_\beta)$ is linear. Therefore we have to show only the convexity of $-\text{tr}(L_s(\rho) \log \rho)$. Since $\{h_{\alpha,\gamma}(\omega)\}$ is a positive matrix we can diagonalize it for every fixed ω . Then (III.19) takes the form

$$L_s(\rho) = \sum_i [V_i, \rho V_i^*] + [V_i \rho, V_i^*] \quad (\text{V.23})$$

where the V_i 's are certain linear combinations of the $V_\alpha(\omega)$'s. Therefore

$$-\text{tr}(L_s(\rho) \log \rho) = 2 \sum_i \{ \text{tr}(V_i^* V_i \rho \log \rho) - \text{tr}(V_i \rho V_i^* \log \rho) \} \quad (\text{V.24})$$

A theorem due to Lieb⁵⁸ asserts that the function

$$\rho \rightarrow -\text{tr}(\rho^q V_i \rho^{1-q} V_i^*) \quad (\text{V.25})$$

$0 \leq q \leq 1$, is convex. For $q = 0$ the function is affine. Therefore the derivative at $q = 0$

$$\rho \rightarrow \text{tr}(V\rho \log \rho V^*) - \text{tr}(\log \rho V\rho V^*) \quad (\text{V.26})$$

is convex. This implies that $-\text{tr} L_s(\rho) \log \rho$ is convex. ■

COMMENTS

1. The technical restriction $\dim \mathcal{H} < \infty$ is annoying and is not overcome easily. Since $S(\rho|\rho_B)$ is quite often infinite, it is difficult to prove that $-S(\Lambda_t \rho|\rho_B)$ is differentiable and that its derivative is given by (V.8). Of course, we can define the entropy production by (V.8) and then all properties stated are still valid. Our theorem holds also for the classical Markov process with finite state space defined by the Pauli equation (III.24) with detailed balance (III.25). For a general classical Markov process with detailed balance^{1,2} one encounters the same difficulties as in the case of an infinite dimensional Hilbert space.

2. Property (ii) is the nonnegativity of the entropy production as required by the phenomenological theory. In general, ρ_B will be the only stationary state. Then $\sigma(\rho) > 0$ for all $\rho \neq \rho_B$. This means that $-S(\rho(t)|\rho_B)$ is strictly increasing reaching in the limit as $t \rightarrow \infty$ the value $-S(\rho_B|\rho_B) = 0$. At $t = 0$, $-S(\rho(t)|\rho_B)$ may have an infinite slope, but at any later time its slope is finite. Typically, this happens if the initial state has, for example, a sharp energy or is otherwise rather pure.

3. Property (iii) is the essential stability property of the entropy production. It guarantees that, as the system is coupled to several reservoirs, there is always a unique state of minimal entropy production. (This statement is too strong. It would be true, if one could prove strict convexity of σ . In general, there is a convex set of states with minimal entropy production.) This situation is analogous to the one in thermodynamics, where the concavity of the entropy ensures stability.

Let us now consider the case of the system $\mathcal{S}$ coupled to reservoirs $\mathcal{R}^1, \dots, \mathcal{R}^r$ at inverse temperatures $\beta_1, \dots, \beta_r$. The time evolution of $\mathcal{S}$ is generated by $L = L_1 + \dots + L_r$. To find a microscopic expression for the entropy production we start again from the balance equation (V.1). The entropy S is still defined by (V.3). The entropy flow is given by

$$J_s = - \sum_{k=1}^r \beta_k dQ_k \quad (\text{V.27})$$

where dQ_k is the heat transfer from the k th reservoir to the system (i.e., the change of energy of S due to the coupling to the k th reservoir). Therefore

$$dQ_k = \text{tr}(\rho L_k^*(H)) \quad (\text{V.28})$$

and, by (V.14),

$$\begin{aligned}
 \sigma(\rho) &= \sum_{k=1}^r -\beta_k \operatorname{tr}(\rho L_k^*(H)) - \operatorname{tr}(L(\rho) \log \rho) \\
 &= \sum_{k=1}^r \{-\beta_k \operatorname{tr}(L_k(\rho)H) - \operatorname{tr}(L_k(\rho) \log \rho)\} \\
 &= \sum_{k=1}^r \sigma_k(\rho)
 \end{aligned} \tag{V.29}$$

The entropy production σ (for a specified state of the system) is the sum of the entropy productions σ_k , where σ_k is the entropy production of $\mathcal{S}$ coupled only to the k th reservoir. As a direct consequence of Theorem 2, we note

Corollary 1. Let $\sigma = \sum_{k=1}^r \sigma_k$. Then $\sigma \geq 0$. Here $\sigma(\rho) = 0$ if and only if $\sigma_k(\rho) = 0$ for $k = 1, \dots, r$. If for every L_k the canonical ensemble ρ_β is the only stationary state (in some temperature region), then $\sigma(\rho) = 0$ if and only if $\beta_1 = \beta_2 = \dots = \beta_r = \beta$ and $\rho = \rho_\beta$.

The entropy production σ is convex.

In the steady state ρ_s , defined by

$$L(\rho_s) = 0, \quad L = L_1 + \dots + L_r \tag{V.30}$$

the entropy production is a bilinear form $\sigma(\rho_s) = \sum_{k=1}^r \beta_k J_k$, where $J_k = \operatorname{tr}(\rho_s L_k^*(H))$ is the steady-state heat flow from the k th reservoir to the system. Since ρ_s depends on $\beta_1, \dots, \beta_r$, J_k does too. We choose some reference temperature β and define the thermodynamic forces by $X_k = -\beta_k + \beta$. Then, using the conservation law $\sum_{k=1}^r J_k = \operatorname{tr}(L(\rho_s)H) = 0$, σ becomes a bilinear form in the fluxes and the thermodynamic forces

$$\sigma(\rho_s) = \sum_{k=1}^r X_k J_k(X_1, \dots, X_r) \tag{V.31}$$

In the *linear* approximation

$$J_k(X_1, \dots, X_r) = \sum_{j=1}^r L_{kj}(\beta) X_j \tag{V.32}$$

and the entropy production is a quadratic form

$$\sigma(\rho_s) = \sum_{k,j=1}^r L_{kj}(\beta) X_k X_j \tag{V.33}$$

The $L_{kj}(\beta)$ are the kinetic coefficients related to the heat conductivities.

From the convexity of σ it follows immediately that

$$\{L_{kj}(\beta)\} \geq 0 \quad (\text{V.34})$$

Since $\{L_{kj}(\beta)\}$ is a matrix on a real vector space, (V.34) does not imply its symmetry $L_{kj} = L_{jk}$ (Onsager relations). As we shall see, however, in Section VII the symmetry essentially follows from the detailed balance property.

VI. APPROACH TO STATIONARITY

On physical grounds one expects that, in general, the reservoir will drive the system to a unique stationary state. Of course, the coupling between the system and the reservoir might be poor (say, $H^{SR} = 0$). Then, since we work in the interaction picture, several stationary states should appear, and, depending on the initial state ρ , $\rho(t)$ should approach one of them as $t \rightarrow \infty$.

Definition 2:

A generator L (or the dynamics $\{e^{Lt}|t \geq 0\}$) is called relaxing, if there exists a unique stationary state ρ_s , $L(\rho_s) = 0$, and if

$$\lim_{t \rightarrow \infty} e^{Lt} \rho = \rho_s \quad (\text{VI.1})$$

for all initial states ρ .

For a single temperature reservoir, the relative entropy is an efficient tool to study the approach to equilibrium. By Theorem 1 $-d/dt S(\rho(t)|\rho_s) > 0$ unless $L(\rho) = 0$. Therefore every initial state ρ tends to a limit as $t \rightarrow \infty$,

$$\lim_{t \rightarrow \infty} e^{Lt} \rho = A_\rho e^{-\beta H} \quad (\text{VI.2})$$

where $A_\rho \in \mathcal{N}$ [cf. (V.19)]. L is relaxing if and only if $\mathcal{N}$ consists only of multiples of the unit operator. In that case the unique stationary state is the canonical ensemble.

One would like to have a condition for relaxation that is more directly related to H and H^{SR} . If we assume that $\{h_{\alpha\gamma}(\omega)\} > 0$ for all $\omega \in \text{Sp}([H, \cdot])$ and all inverse temperatures β , then $\mathcal{N} = \{V_\alpha(\omega)|\alpha, \omega \in \text{Sp}([H, \cdot])\}'$. ' denotes the set of all operators commuting with the ones in $\{\cdot\}$ [i.e., $\mathcal{N}$ is the set of all operators commuting with all $V_\alpha(\omega)$'s]. If, furthermore, $\{H, V_\alpha|\alpha\}' = \{\mathbb{C}1\}$, then, as can be shown,⁵⁷ $\mathcal{N} = \{\mathbb{C}1\}$. Hence $\{h_{\alpha\gamma}(\omega)\} > 0$ and $\{H, V_\alpha|\alpha\}' = \{\mathbb{C}1\}$ is a sufficient condition for relaxation. In the case of several reservoirs at different temperatures one can use the fact

that, if $L_1, \dots, L_r$ are relaxing, then also $L = L_1 + \dots + L_r$ is relaxing ($\dim \mathcal{H} < \infty$).

For the case of an infinite dimensional Hilbert space one has to use much more powerful methods than we introduced so far to prove⁶⁰ (cf. also Refs. 59, 61–63).

Theorem 3. Let the dynamics of $\mathcal{S}$ coupled to the reservoirs $\mathcal{R}^1, \dots, \mathcal{R}^r$ be given by the generator $L = L_1 + \dots + L_r$ as in (III.29). If for given inverse temperatures $\beta_1, \dots, \beta_r$ $\{h_{\alpha\gamma}^{(k)}(\omega)\} > 0$ for all $\omega \in \text{Sp}([H, \cdot])$, $k = 1, \dots, r$, and if

$$\{H, V_\alpha^{(k)}|_{\alpha}, k = 1, \dots, r\}' = \{\mathbb{C}1\} \quad (\text{VI.3})$$

(i.e., only multiples of the unit operator commute with H and the $V_\alpha^{(k)}$'s), then L is relaxing.

Remark: For readers who did not omit Section IV. Theorem 3 is the special case of a very fine theorem.⁶⁰ Let $\{\Lambda_t^*|t \geq 0\}$ be a quantum-dynamical semigroup with generator L^* . Then we define the dissipation function⁵¹ $D: B(\mathcal{H}) \times B(\mathcal{H}) \rightarrow B(\mathcal{H})$ by

$$D(A, B) = L^*(A^*B) - L^*(A^*)B - A^*L^*(B) \quad (\text{VI.4})$$

One shows that $D(A, A) \geq 0$. If $D(A, A) = 0$ for all A , then $L^*(A) = i[H, A]$, which means that there is no dissipation at all. Obviously, $D(1, 1) = 0$. The theorem of Frigerio states that if $D(A, A) = 0$ implies $A = c1$, then $\{\Lambda_t^*|t \geq 0\}$ is relaxing. In this case we have complete dissipation. Therefore the dissipation function D characterizes the lack of reversibility of L^* . Using the form (IV.6) of the generator L^* , the preceding condition is equivalent to $\{V_j|j \in I\}' = \{\mathbb{C}1\}$.

Theorem 3 gives us a physically very intuitive criterion for an effective coupling, causing the system to approach a unique steady state. $\{h_{\alpha\gamma}^{(k)}(\omega)\} > 0$ means that the reservoir couples to all relevant frequencies of $\mathcal{S}$ and (VI.3) expresses that, besides the unit operator, there is no other operator that commutes with the Hamiltonian H and the interaction operators $V_\alpha^{(k)}$. To put it somewhat differently: If we form arbitrary linear combinations and products of H and the $V_\alpha^{(k)}$'s (and take weak limits), then we obtain in this way any bounded operator, which means that H and the $V_\alpha^{(k)}$'s together have to be sufficiently incompatible.

VII. ONSAGER RELATIONS

We show the validity of the Onsager relations⁶⁴

$$L_{kj}(\beta) = L_{jk}(\beta) \quad (\text{VII.1})$$

[cf. (V.33)], for the system $\mathcal{S}$ weakly coupled to several reservoirs. In the special case of the Pauli master equation (III.24), Hepp^{65,66} proved (VII.1) using the derivation of the Onsager relations for a classical system coupled to stochastic reservoirs as given by Bergmann, Lebowitz et al.^{1,67}

Let $\rho_s = \rho_s(\beta_1, \dots, \beta_r)$ be the unique stationary state of the generator $L = L_{1,\beta_1} + \dots + L_{r,\beta_r}$, where we indicated explicitly the temperature dependence of the k th generator. Then the kinetic coefficients $L_{kj}(\beta)$ are defined by

$$L_{kj}(\beta) = \frac{\partial}{\partial \beta_j} \text{tr} [L_{k,\beta_k}(H) \rho_s(\beta_1, \dots, \beta_r)]|_{(\beta_1, \dots, \beta_r) = (\beta, \dots, \beta)} \quad (\text{VII.2})$$

$k \neq j$. By the conservation law $\sum_k \text{tr} (L_k^*(H) \rho_s) = 0$, $L_{jj}(\beta) = -\sum_{k \neq j} L_{kj}(\beta)$. Our proof of (VII.1) consists of two steps: First, we derive a convenient expression for the kinetic coefficients $L_{kj}(\beta)$ and then show their symmetry. The essential ingredient of the proof is the detailed balance property (III.27), which was a direct consequence of the KMS condition for the thermal equilibrium state of the reservoirs.

Lemma 1. Let $\dim \mathcal{H} < \infty$. Let the operator for the heat flow from the k th reservoir at inverse temperature β_k to the system be $J_{k,\beta_k} = L_{k,\beta_k}^*(H)$ and let $L_{1,\beta_1} + \dots + L_{r,\beta_r}$ have a unique stationary state $\rho_s(\beta_1, \dots, \beta_r)$ in some neighborhood of $(\beta, \dots, \beta)$. Then the kinetic coefficients $L_{kj}(\beta)$ are given by

$$L_{kj}(\beta) = -\text{tr} \left[\frac{1}{L^*} (J_{k,\beta} J_{j,\beta} \rho_\beta) \right] \quad (\text{VII.3})$$

$$= \int_0^\infty dt \text{tr} [J_{k,\beta}(t) J_{j,\beta} \rho_\beta] \quad (\text{VII.4})$$

with $J_{k,\beta}(t) = e^{L^* t} J_{k,\beta}$ and $L = L_{1,\beta} + \dots + L_{r,\beta}$.

Proof: Since the canonical ensemble ρ_β is invariant for $L_{j,\beta}$, we have

$$L'_{j,\beta}(\rho_\beta) = L_{j,\beta}(H \rho_\beta) = J_{j,\beta} \rho_\beta \quad (\text{VII.5})$$

where ' denotes the derivative with respect to β and where we used $L_{a,k}(H) = 0$ and the detailed balance (III.27) for $L_{s,k}$. Since $\rho_s(\beta, \dots, \beta) = \rho_\beta$

$$(L_{1,\beta} + \dots + L_{j,\beta+\delta} + \dots + L_{r,\beta})(\rho_s(\beta, \dots, \beta + \delta, \dots, \beta)) - L(\rho_\beta) = 0 \quad (\text{VII.6})$$

which implies

$$L'_{j,\beta}(\rho_\beta) = -L(\rho'_s(\beta)) \quad (\text{VII.7})$$

and, by (VII.5),

$$L(\rho'_s(\beta)) = -J_{i,\beta}\rho_\beta \quad (\text{VII.8})$$

Since, by assumption, the kernel of L is one-dimensional (i.e., the eigenvalue zero is nondegenerate), (VII.8) admits the one-parameter family of solutions

$$\rho'_s(\beta) = c\rho_\beta - \frac{1}{L}(J_{i,\beta}\rho_\beta) \quad (\text{VII.9})$$

$c \in \mathbb{R}$, which defines $(1/L)(J_{i,\beta}\rho_\beta)$. Since $\text{tr}(J_{k,\beta}\rho_\beta) = 0$,

$$L_{kl}(\beta) = -\text{tr} \left[J_{k,\beta} \frac{1}{L}(J_{i,\beta}\rho_\beta) \right] \quad (\text{VII.10})$$

ρ_β is the only stationary state of L . By the discussion in Section VI this implies that $\lim_{t \rightarrow \infty} e^{Lt}(J_{i,\beta}\rho_\beta) = c\rho_\beta$ and that, except zero, all eigenvalues of L lie in the open left-hand plane. Therefore we can express the inverse in (VII.10) as Laplace transform

$$L_{kl}(\beta) = \int_0^\infty dt \text{tr} [J_{k,\beta} e^{Lt}(J_{i,\beta}\rho_\beta)] \quad (\text{VII.11})$$

where we used again $\text{tr}(J_{k,\beta}\rho_\beta) = 0$. The integral (VII.11) is finite. ■

It is no coincidence that (VII.4) looks like the well-known Kubo formula for transport coefficients. One can derive (VII.4) in the framework of linear response theory adapted to our model.^{4,68}

Theorem 4. Let $\dim \mathcal{H} < \infty$ and let L_a and L_s be the antisymmetric and the symmetric part of $L = L_{1,\beta_1} + \dots + L_{r,\beta_r}$. If in some neighborhood of $(\beta, \dots, \beta)$ the unique stationary state ρ_s of L is also the unique stationary state of L_s , then the Onsager relations (VII.1) are valid.

Proof: Since the stationary state is already defined by $L_s(\rho_s) = 0$, we can repeat the derivation of (VII.4) with L_s instead of L and obtain (VII.4) with L replaced by L_s . By the detailed balance property (III.27)

$$e^{L_s t}(A\rho_\beta) = e^{L_s^* t}(A)\rho_\beta \quad (\text{VII.12})$$

Since $[J_{k,\beta}, \rho_\beta] = 0$

$$\text{tr} [e^{L_s^* t}(J_{k,\beta})J_{i,\beta}\rho_\beta] = \text{tr} [e^{L_s t}(J_{i,\beta})J_{k,\beta}\rho_\beta] \quad (\text{VII.13})$$

which implies (VII.1). ■

The conditions of the theorem are certainly met, when $L_a = 0$. They are also fulfilled, whenever the spectrum of H is nondegenerate. Since the free

time evolution commutes with e^{Lt} and since ρ_s is unique

$$[H, \rho_s] = 0 \quad (\text{VII.14})$$

In general, this does not imply $L_a(\rho_s) = 0$. However, if the spectrum of H is nondegenerate, then ρ_s is a function of H and therefore $L_a(\rho_s) = 0$. In general, one obtains

$$\text{tr} [e^{(L_a^* + L_a^*)t} (J_{k,\beta}) J_{j,\beta} \rho_\beta] = \text{tr} [e^{(L_a^* - L_a^*)t} (J_{j,\beta}) J_{k,\beta} \rho_\beta] \quad (\text{VII.15})$$

Without additional assumptions (VII.15) does not imply the Onsager relations (VII.1).

At first sight it is somewhat surprising that the Onsager relations should not be valid in full generality. The reason is to be sought in our construction of the generator L . If we consider L as a function of the Hamiltonian H , then L is discontinuous whenever two eigenvalues meet. (This is so, since the projection P_i on the eigenspace for the energy ε_i changes discontinuously.) There is, however, a unique way to extend L continuously through the points of discontinuity. If we choose this (at finitely many points) modified $\tilde{L}$ as generator of the time evolution, then all our results remain valid and the Onsager relations hold without any restriction.

Remark: The reader will have noticed that we used the assumption $\dim \mathcal{H} < \infty$, which is, in view of physical applications, rather restrictive. The present theorem generalizes to infinite dimensional Hilbert spaces. Since we assumed the partition function to be finite, H is necessarily unbounded. Therefore the heat flow $L^*(H)$ (properly defined) becomes unbounded and one has to be somewhat careful with the integral (VII.4). For clarity and brevity of the argument, we thought it best to avoid such technicalities.

VIII. PRINCIPLE OF MINIMAL ENTROPY PRODUCTION

In the phenomenological theory the steady state may be characterized, under certain conditions, by a minimum of the entropy production compatible with the external constraints imposed on the system.⁶⁹⁻⁷¹ This property is valid only if the fluxes are proportional to the thermodynamic forces (i.e., only in the linear regime). As an illustration we consider the case of thermal conduction, where the entropy production as given by irreversible thermodynamics is [cf. (V.2)]

$$\sigma = \int \mathbf{J} \cdot \text{grad} \frac{1}{T} dV = \int L_{qq} \left(\text{grad} \frac{1}{T} \right)^2 dV \quad (\text{VIII.1})$$

in the linear approximation with $\mathbf{J} = L_{qq} \text{grad } 1/T$. For fixed boundary

conditions the minimum of σ is given by

$$\Delta \frac{1}{T} = 0 \quad (\text{VIII.2})$$

which implies

$$\frac{\partial}{\partial t} T = 0 \quad (\text{VIII.3})$$

by the heat equation $(\partial/\partial t)T = \alpha \Delta T$.

In our model the stationary states are defined by $L(\rho) = 0$. They form a convex set (any convex combination of stationary states is stationary). The states of minimal entropy production are defined by $\sigma(\rho)$ minimal. By the convexity of σ they also form a convex set. The external constraints are already specified by the reservoir temperatures appearing in L and σ . In analogy to the phenomenological theory it is tempting to conjecture

$$L(\rho) = 0 \Leftrightarrow \sigma(\rho) = \text{minimal} \quad (\text{VIII.4})$$

If all reservoir temperatures are the same, (VIII.4) has been proved in Theorem 2. If the reservoir temperatures are different, one can show by explicit examples (e.g., $\dim \mathcal{H} = 2$) that (VIII.4) is not true in general. From our preceding discussion this should come as no surprise, since for any finite temperature difference we are already in the nonlinear regime (the steady-state heat flow is not proportional to the temperature difference, in general). To derive the principle of minimal entropy production we have to proceed in a somewhat different way.

Let $L = L_{1,\beta_1} + \dots + L_{r,\beta_r}$ have a unique stationary state $\rho_s(\beta_1, \dots, \beta_r)$ in some neighborhood of $(\beta, \dots, \beta)$. We then expand

$$\rho_s(\beta_1, \dots, \beta_r) = \rho_\beta + \sum_{k=1}^r \rho_{s,k}(\beta)(\beta_k - \beta) + \dots \quad (\text{VIII.5})$$

Similarly, let $\sigma = \sigma_{1,\beta_1} + \dots + \sigma_{r,\beta_r}$ have a unique minimum $\rho_m(\beta_1, \dots, \beta_r)$. By convexity and the smooth dependence of σ_{k,β_k} on β_k , $\rho_m(\beta_1, \dots, \beta_r)$ depends smoothly on the inverse temperatures. Furthermore, by Theorem 1, $\rho_m(\beta, \dots, \beta) = \rho_\beta$. We expand

$$\rho_m(\beta_1, \dots, \beta_r) = \rho_\beta + \sum_{k=1}^r \rho_{m,k}(\beta)(\beta_k - \beta) + \dots \quad (\text{VIII.6})$$

Then the principle of minimal entropy production asserts that

$$\rho_{m,k}(\beta) = \rho_{s,k}(\beta) \quad (\text{VIII.7})$$

for $k = 1, \dots, r$ [i.e., (VIII.4) is valid in the linear approximation].

Theorem 5. Let $\dim \mathcal{H} < \infty$ and let the spectrum of H be nondegenerate. Let $L_{1,\beta_1} + \dots + L_{r,\beta_r}$ have a unique stationary state $\rho_s(\beta_1, \dots, \beta_r)$ and σ_{r,β_r} have a unique minimum $\rho_m(\beta_1, \dots, \beta_r)$ in some neighborhood of $(\beta_1, \dots, \beta_r)$. Then

$$\rho_{m,k}(\beta) = \rho_{s,k}(\beta) \quad (\text{VIII.7})$$

Proof: In Lemma 1 we showed that $\rho_{s,k}(\beta)$ is defined by

$$L(\rho_{s,k}(\beta)) = -L_{k,\beta}^*(H)\rho_{\beta}, \quad (\text{VIII.8})$$

where $L = L_{1,\beta} + \dots + L_{r,\beta}$ (VII.8).

Let $U(t) = e^{-iHt}$. Then

$$\begin{aligned} \sigma_{k,\beta_k}(U(t)\rho U(t)^*) &= -\text{tr}[U(t)L_{k,\beta_k}(\rho)U(t)^*U(t)(\log \rho + \beta_k H)U(t)^*] \\ &= \sigma_{k,\beta_k}(\rho) \end{aligned} \quad (\text{VIII.9})$$

Therefore, since the minimal state is unique by assumption,

$$[\rho_m(\beta_1, \dots, \beta_r), H] = 0 \quad (\text{VIII.10})$$

Since the spectrum of H is nondegenerate, ρ_m is a function of H . Therefore it suffices to study the minimum of σ amongst the states diagonal in the energy basis $\{\Psi_j | j = 1, \dots, \dim \mathcal{H}\}$.

We consider σ as a function of the eigenvalues ρ_j of ρ . Then the minimum of σ is defined by

$$\frac{\partial}{\partial \rho_j} \sigma(\rho) = 0 = - \sum_{i=1}^r \left\{ \text{tr}(L_{i,\beta_i}(\rho_j)(\log \rho + \beta_i H) + \langle \Psi_j | L_{i,\beta_i}(\rho) \Psi_j \rangle \frac{1}{\rho_j} \right\} \quad (\text{VIII.11})$$

where $L_{i,\beta_i}(\rho_j) = L_{i,\beta_i}(\rho_j) |\Psi_j\rangle \langle \Psi_j|$ and $\rho = \rho_m(\beta_1, \dots, \beta_r)$. By Theorem 1, $\sigma_{k,\beta+\delta}(\rho_{\beta+\delta}) = 0$. Taking the derivative at $\delta = 0$

$$\langle \Psi_j | L'_{k,\beta}(\rho_{\beta}) \Psi_j \rangle - \langle \Psi_j | L'_{k,\beta}(H\rho_{\beta}) \Psi_j \rangle = 0 \quad (\text{VIII.12})$$

for all j , where ' denotes the derivative with respect to δ at $\delta = 0$. In (VIII.11) we choose now $(\beta_1, \dots, \beta_k, \dots, \beta_r) = (\beta, \dots, \beta + \delta, \dots, \beta)$ and we obtain by taking the derivative at $\delta = 0$

$$\begin{aligned} \sum_{i \neq k} \text{tr} \left[L_{i,\beta}(\rho_{\beta,i}) \frac{1}{\rho_{\beta}} \rho_{m,k}(\beta) \right] + \text{tr} \left[L_{k,\beta}(\rho_{\beta,i}) \left(\frac{1}{\rho_{\beta}} \rho_{m,k}(\beta) + H \right) \right] \\ + \sum_{i=1}^r \langle \Psi_j | L_{i,\beta}(\rho_{m,k}(\beta)) \Psi_j \rangle \frac{1}{\rho_{\beta,i}} + \langle \Psi_j | L'_{k,\beta}(\rho_{\beta}) \Psi_j \rangle \frac{1}{\rho_{\beta,i}} = 0 \end{aligned} \quad (\text{VIII.13})$$

for all j , where $\rho_{\beta,j}$ is the j th eigenvalue of ρ_{β} . Inserting (VIII.12), we obtain

$$\begin{aligned} \left\langle \Psi_j \right| \left\{ \sum_{l=1}^r L_{l,\beta}(\rho_{m,k}(\beta)) + L_{k,\beta}^*(H)\rho_{\beta} \right\} \Psi_j \rangle + \rho_{\beta,j}^2 \left\langle \Psi_j \right| \left\{ \sum_{l \neq k} L_{l,\beta}^* \left(\frac{1}{\rho_{\beta}} \rho_{m,k}(\beta) \right) \right. \\ \left. + L_{k,\beta}^* \left(\frac{1}{\rho_{\beta}} \rho_{m,n}(\beta) + H \right) \right\} \Psi_j \rangle = 0 \quad (\text{VIII.14}) \end{aligned}$$

The second term can be rewritten as

$$L^* \left(\frac{1}{\rho_{\beta}} \rho_{m,k}(\beta) \right) + L_{k,\beta}^*(H) = \frac{1}{\rho_{\beta}} L(\rho_{m,k}(\beta)) + L_{k,\beta}^*(H) \quad (\text{VIII.15})$$

where we used the detailed balance property (III.27) and the fact that $L_a(f(H)) = 0$ for any function f of H . Therefore (VIII.14) vanishes for

$$L(\rho_{m,k}(\beta)) = -L_{k,\beta}^*(H)\rho_{\beta} \quad \blacksquare \quad (\text{VIII.16})$$

Concerning the technical restrictions in Theorem 5, the same remarks as before apply. If we define the entropy production by (V.8), then the theorem is also valid for an infinite dimensional Hilbert space.

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